Heat capacity of pure and alloyed plutonium

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I. MOTIVATION

Thermodynamics of Pu and its alloys has been studied both experimentally and theoretically since the time of the Manhattan project and yet after more than fifty years of extensive research some fundamental questions still await explanation. Among the most puzzling is the mechanism of stabilization of the high-temperature fcc δ-phase of Pu down to very low temperatures by alloying with certain trivalent elements such as Al, Ga, Ce, Am, In, etc. Related to this is the origin of a negative thermal expansion of δ-Pu that becomes zero and eventually positive upon alloying Pu with Al or Ga that locally compress the lattice or Ce and Am that cause the expansion of the lattice.

II. THERMODYNAMIC ANALYSIS

Theoretical investigation of the thermodynamics of Pu and its dilute alloys relies on an accurate formulation of the total free energy that is commonly written as $F(T) = \Phi_0(x) + F_p(T,x) + F_e(T,x)$, where T is the absolute temperature and x the atomic concentration of the alloying element in Pu (e.g. Al, Ga, Ce, Am). Here, Φ_0 is the internal energy of the crystal with atoms at the equilibrium lattice sites and its electrons in the ground state, $F_p = F_{p(h)} + F_{p(a)}$ the phonon contribution due to harmonic and anharmonic lattice vibrations and F_e the electronic contribution from states with energy $\pm kT$ about the Fermi energy. The temperature dependence of the free energy F is dominated by the harmonic phonon contribution, $F_{p(h)}$, and the electronic contribution, F_e, which accounts to as much as $(10-20)\%$ of the total free energy. The anharmonic effects play role only at high temperatures and even at these temperatures represent at most about 5% of the free energy; this contribution will not be discussed in the following.

Knowing the expression for the free energy, one can easily obtain the heat capacity as $c_V(T,x) = -T(\partial^2 F/\partial T^2)_V$, which suggests writing the heat capacity as $c_V(T,x) = c_V^p(T,x) + c_V^e(T,x)$, where c_V^p is the heat capacity due to harmonic phonons and c_V^e the electronic contribution. At low temperatures, i.e. when

$\hbar\omega >> kT$ for any phonon frequency ω, wavelengths of the harmonic phonons are long compared to the lattice parameter and the crystal can be accurately approximated as a continuous medium. The phonon part of the heat capacity then reads

$$c_V^p(T,x) = \frac{12\pi^4}{5} Nk \left(\frac{T}{\theta_D(x)}\right)^3 \qquad \text{for } \hbar\omega >> kT \ . \tag{1}$$

At high temperatures, on the other hand, phonon wavelength becomes comparable to the interatomic spacing and the phonons probe the crystalline nature of the lattice. In this limit ($\hbar\omega << kT$), phonons occupations follow from the Bose-Einstein distribution and the leading order high-temperature expansion of the harmonic free energy is then

$$c_V^p(T,x) = 3Nk \left[1 - \frac{1}{20}\left(\frac{\theta_2(x)}{T}\right)^2\right] \qquad \text{for } \hbar\omega << kT \ . \tag{2}$$

The electronic heat capacity can be derived from the Sommerfeld model in which individual electronic states are distributed according to the Fermi-Dirac statistics. Expanding the chemical potential about the Fermi energy ϵ_F, one arrives at

$$c_V^e(T,x) = \frac{\pi^2}{3} k^2 T n(\epsilon_F, x) \left\{1 - \frac{\pi^2}{6}(kT)^2 \left[\frac{n'(\epsilon_F, x)}{n(\epsilon_F, x)}\right]^2\right\} \ , \tag{3}$$

where $n(\epsilon_F, x)$ is the electronic density of states at the Fermi energy, and $n'(\epsilon_F, x)$ its slope. In Pu and its alloys, recent photoemission experiments [1] reveal that $n(\epsilon_F, x)$ for Pu and its alloys are sharply peaked at the Fermi level and, therefore, at high temperatures one cannot neglect the correction term in (3).

III. CALCULATION OF THERMODYNAMIC PARAMETERS FROM EXPERIMENTS

At low temperatures, the heat capacity can be written from (1) and (3) as $c_V/T = \alpha T^2 + \gamma$, where α determines the Debye temperature $\theta_D(x)$, and γ is the Sommerfeld coefficient that is proportional to the electronic density of states at the Fermi energy, $n(\epsilon_F, x)$.

Although experimental measurements of the heat capacity are performed at constant pressure, low-temperature thermal expansion of Pu and its dilute alloys is negligible. Hence, one may safely consider $c_P \approx c_V$ and the parameters α and γ can be obtained from low-temperature data for $c_P(T)$. Using this technique, Lashley et al. [2] revealed that γ for Pu+5at%Al is almost a factor of four higher than that of pure α-Pu.
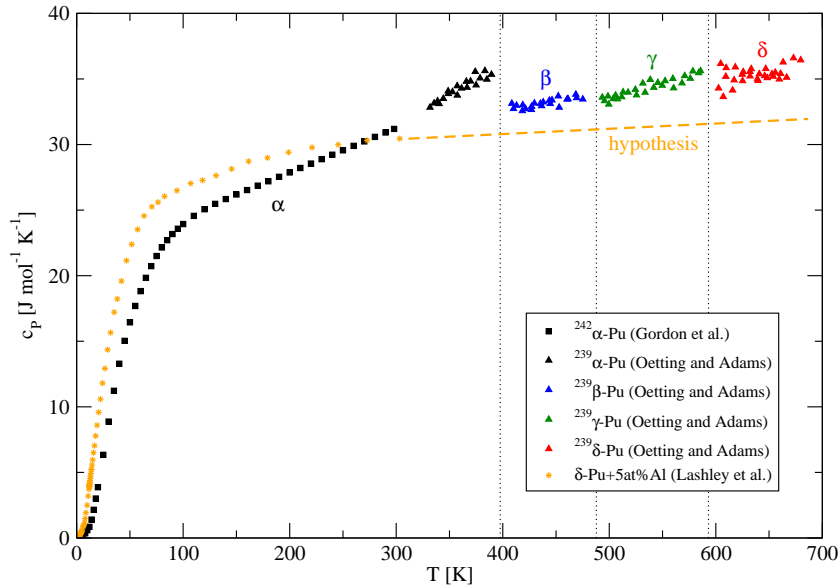

FIG. 1: Heat capacity of pure Pu (α, β, γ, δ phases) and of Pu+5at%Al. No experimental data on Pu+5at%Al exist at high temperatures and so the dashed line represents a hypothetical continuation of the low-temperature data.

At high temperatures, the phonon contribution approaches the Dulong-Petit limit $3Nk$ and the slope of the $c_P(T)$ data is determined purely by the electronic contribution. In Fig. 1, we show the experimentally measured heat capacity for various phases of pure Pu and for Pu+5at%Al. The slope of the $c_P(T)$ data for pure Pu is higher than that for the Pu alloy which is opposite to the trend observed at low temperatures. While addition of Al increases c_P^e at low temperatures, it causes its decrease at high temperatures. Similar observations were made on Pu-Ga alloys. From experiments of Taylor et al. [4] and Rose et al. [3], one learns that the electronic heat capacity of Pu-Ga alloys above 300 K first increases for up to 3.2at%Ga and then drops for 5at%Ga. Further understanding of the effect of alloying on the heat capacity of Pu requires: (i) measurements of the heat capacity on Pu+5at%Al above 300 K, (ii) measurements of the heat capacity for Pu-Al alloys with concentration of Al other than 5at%. These experiments would resolve the trend in c_P^e and allow accurate construction of the free energy.

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[2] Lashley, J., Singleton, J., Migliori, A., Betts, J., Fisher, R., Smith, J., and McQueeney, R. (2003). Experimental electronic heat capacities of α- and δ-plutonium: Heavy-fermion physics in an element. *Phys. Rev. Lett.*, 91(20):205901.

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